Resin Glycosides. XV.[1] Simonins I—V, Ether-Soluble Resin Glycosides (Jalapins) from the Roots of *Ipomoea batatas* (cv. Simon)

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Five new ether-soluble resin glycosides (jalapins), simonins I—V, have been isolated from the roots of *Ipomoea batatas* and characterized on the bases of chemical and spectral data. Simonin I is the first example of resin glycoside with aromatic acid (*trans*-cinnamic acid) as a component organic acid.

Keywords resin glycoside; jalapin; *Ipomoea batatas* (cv. Simon); Convolvulaceae; simonin; *trans*-cinnamic acid; simonic acid A; simonic acid B

The roots of *Ipomoea batatas* (L.) LAM. (cv. Simon), Convolvulaceae, known as Batata Simao Brazil, are used for food and as a folk medicine in Minas Gerais, Brazil. Since 1973, the plant has been cultivated as a health food in western Japan. Yang claimed that the roots and leaves were effective for leukemia, anemia, hypertension, diabetes and hemorrhage.[2] Recently, Kawanishi *et al.* reported the occurrence of a mixture of hexa-, hepta and octa-decyl ferulates in the roots.[3]

As to the resin glycoside of this species, Lee *et al.* obtained a mixture of jalapin from the tuber of Korean *I. batatas*, and proposed a tentative structure, that is, jalapinolic acid 11-*O*-L-rhamnofuranosyl-(1→4)-D-fucopyranosyl-(1→3)-D-glucopyranoside, probably esterified with lower acids.[4] As a part of our chemical studies on the resin glycosides characteristic of Convolvulaceae plants, we have examined the roots of this plant and isolated five new jalapins named simonins I—V. This paper deals with the isolation and structural elucidation of these compounds.

The $CHCl_3$ extract of the dry roots was partitioned between *n*-hexane and MeOH to afford a jalapin like fraction in the yield of 0.016%. In order to examine the presence of resin glycoside, the fraction was subjected to alkaline and acidic hydrolyses, successively. Gas chromatographic (GC) analysis of the ether-soluble fraction of the alkaline hydrolysis product demonstrated the presence of isobutyric, 2-methylbutyric, tiglic, *n*-octanoic, *n*-decanoic, *n*-dodecanoic and *trans*-cinnamic acids. The configuration at C-2 of the 2-methylbutyric acid was defined as *S* by Helmchen's method.[5] Acidic hydrolysis of the ether-insoluble fraction gave jalapinolic acid and a monosaccharide mixture. The chirality at C-11 of the former was determined to be *S* according to Mosher's method.[6] The monosaccharide mixture was found to consist of D-glucose, D-fucose and L-rhamnose by GC according to Hara *et al.*[7] These data suggested that the fraction contains some resin glycosides, in particular, one with an aromatic acid (cinnamic acid) not previously known as a component organic acid of resin glycosides.

Column chromatography and subsequent preparative high-performance liquid chromatography (HPLC) of the fraction afforded simonins I (**1**), II (**2**), III (**3**), IV (**4**) and V (**5**).

Simonin I (**1**), $C_{69}H_{112}O_{21}$, negative ion fast atom bombardment mass spectrum (FAB-MS) *m/z*: 1275 $[M-H]^-$, showed the signals of four ester carbonyl, two olefinic and six aromatic carbons in the ^{13}C-NMR spectrum (Table I). On alkaline hydrolysis followed by methylation with diazomethane, **1** yielded methyl *n*-decanoate, methyl *trans*-cinnamate and the methyl ester of operculinic acid C[8] (**6**), *viz.* (*S*)-jalapinolic acid 11-*O*-α-L-rhamnopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→2)-α-D-fucopyranoside, obtained previously from *Jalapae Braziliensis*.[9]

The ^1H-NMR spectrum of **1** showed, besides the signals of olefinic (δ 6.50, 7.79, each 1H, d, $J=15.9$ Hz) and phenyl protons (δ 7.25—7.50, 5H) due to the *trans*-cinnamic acid group (Cna), the signals of nonequivalent 2-H_2 of the

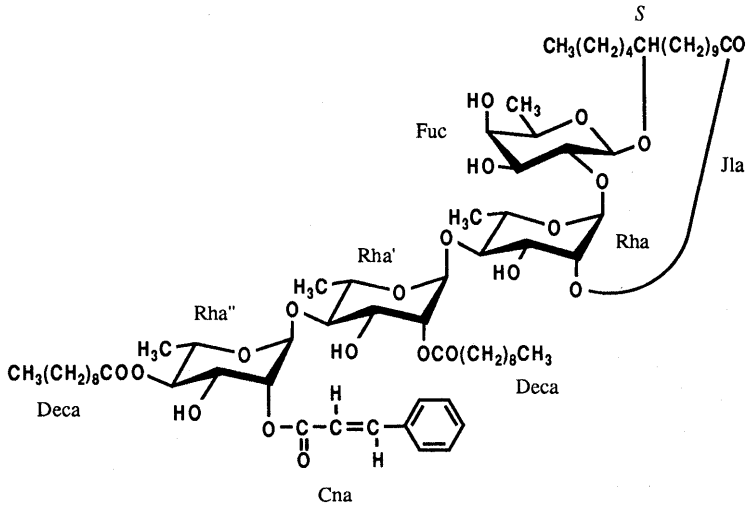

Fig. 1. Structure of **1**

TABLE I. ^{13}C-NMR Spectral Data for **1**, **2**, **3**, **4**, **5**, **7** and **8** (in Pyridine-d_5)

		1	**2**	**7**	**3**	**8**	**4**	**5**
Fuc	1	104.7			104.3	101.2	104.3	104.3
	2	80.1			80.3	74.9	80.3	80.3
	3	73.6			73.3	76.7	73.3	73.4
	4	73.0			72.9	73.5	72.9	72.9
	5	70.7			70.8	71.2	70.8	70.8
	6	17.4			17.3	17.2	17.3	17.3
Glc	1		104.5	101.0				
	2		82.8	79.7				
	3		76.5	76.9				
	4		71.9	72.2				
	5		82.1	78.2				
	6		62.8	62.9				
Rha	1	98.7	98.8	101.3	98.8	101.4	98.8	98.8
	2	73.8	73.7	73.2	73.9	73.2	73.9	73.9
	3	69.9	70.0	72.2	69.9	72.7	69.8	69.8
	4	81.2	80.0	80.5	80.1	80.2	79.8	80.1
	5	68.8	68.5	67.3	70.5	67.1	70.7	68.6
	6	19.4	18.9	19.2	19.4	18.9	19.4	19.4
Rha′	1	100.3	99.1	102.9	99.2	102.9	99.2	99.2
	2	74.1	73.0	72.1	73.1	72.0	73.2	73.2
	3	70.9	79.9	82.6	79.5	82.6	79.4	79.8
	4	80.2	79.7	78.7	80.1	78.7	80.1	79.4
	5	68.4	68.7	68.8	68.5	68.7	68.2	68.2
	6	18.9	19.4	18.3	18.8	18.3	18.8	18.8
Rha″	1	100.5	104.9	104.5	104.8	103.3	104.6	104.6
	2	74.2	72.5	72.7	72.5	72.7	72.5	72.6
	3	68.3	72.6	72.7	72.5	72.8	72.5	72.5
	4	75.3	73.5	73.7	73.5	74.0	73.6	73.6
	5	68.2	70.4	70.1	68.6	70.4	68.5	68.5
	6	18.1	17.9	18.6	18.5	18.6	18.5	18.5
Rha‴	1		103.2	103.4	103.7	104.5	103.5	103.5
	2		72.7	72.7	72.5	72.7	72.6	72.6
	3		70.3	72.8	70.2	72.8	70.3	70.3
	4		75.1	74.0	75.1	73.7	75.1	75.1
	5		68.2	70.4	68.2	70.1	68.6	68.2
	6		18.8	18.9	17.9	18.6	18.8	17.9
Jla	11	82.5	77.9	78.2	82.3	78.0	82.4	82.4
	16	14.3	14.2	14.4	14.5	14.4	14.3	14.3
Cna	7	118.7						
	8	128.6						
		129.2 (×2)						
		130.7 (×2)						
		135.2						
		149.5						
	9	166.4						
Org	1	173.1	173.4	174.0	173.1	174.1	172.9	172.9
		173.3	173.5		173.5		173.1	173.1
		173.7	175.5		175.5		173.5	173.5
OCH_3				51.3		49.7		

δ in ppm from tetramethylsilane (TMS). All the chemical shifts are based on the heteronuclear shift correlated 2D-NMR (HETCOR) spectral data. Org: octanoyl, decanoyl or dodecanoyl.

jalapinolic acid moiety (Jla) together with those of two 2-H_2 (δ 2.32, 2.44, each 2H) of *n*-decanoic acid groups (Deca) (Table II), suggesting that **1** consists of 1 mol each of operculinic acid C and *trans*-cinnamic acid, and 2 mol of *n*-decanoic acid, and that **1** has a macrocyclic ester structure similar to those of jalapins so far isolated. In a comparison of the ^{1}H-NMR spectrum with that of **6**, the signals due to 2-H of the first rhamnose (Rha), 2-H of the second rhamnose (Rha′), and 2-H and 4-H of the third rhamnose (Rha″) were observed at lower field than those of **6**[8] by 1.34, 1.33, 1.49 and 1.63 ppm, respectively. In addition, the negative ion FAB-MS of **1** exhibited fragment peaks at *m/z* 1145 $[M-H-130\ (Cna)]^-$, 837 $[1145-154\ (Deca)\times 2]^-$, 691 $[837-146\ (methylpentose\ unit)]^-$, 545 $[691-146]^-$, 417 $[545-146+18\ (H_2O)]^-$, 271 $[417-146,\ Jla]^-$. The fragment ions of *m/z* 545 and 417 implied that the ester linkage of Jla involves Rha, linked at its 2-OH.[10]

The sites of the ester linkages of Cna and the two Deca were defined by use of ^{1}H detected heteronuclear multiple bond multiple quantum coherence (HMBC) spectroscopy.[11] In the spectrum of **1**, among four ester carbonyl carbon signals, the signal at δ 166.4 correlated with those of the olefinic protons due to Cna as well as with that of 2-H of Rha″. The site of Cna is therefore at 2-OH of Rha″ and hence the remaining two Deca are located at 2-OH of Rha′ and 4-OH of Rha″.

Accordingly, the structure of simonin I (**1**) was concluded to be (*S*)-jalapinolic acid 11-*O*-(2-*O*-*trans*-cinnamoyl)-[(4-*O*-*n*-decanoyl)]-α-L-rhamnopyranosyl-(1→4)-*O*-(2-*O*-*n*-decanoyl)-α-L-rhamnopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-fucopyranoside, intramolecular 1, 2″-ester (Fig. 1).

Simonin II (**2**), $C_{63}H_{110}O_{25}$, negative ion FAB-MS *m/z*: 1265 $[M-H]^-$), showed, in the ^{13}C-NMR spectrum, the signals of five anomeric and three ester carbonyl carbons (Table I). Alkaline hydrolysis of **2** followed by methylation in the same manner as for **1** gave methyl (*S*)-2-methylbutyrate, methyl *n*-dodecanoate and the methyl ester of a new glycosidic acid named simonic acid A (**7**), $C_{47}H_{84}O_{24}$.

The negative ion FAB-MS of **7** showed the $[M-H]^-$ ion peak at *m/z* 1031 and fragment peaks at *m/z* 885 $[1031—146\ (methylpentose\ unit)]^-$, 739 $[885-146]^-$, 593 $[739-146]^-$, 415 $[593-146-32\ (CH_3OH)]^-$, 253 $[415-162\ (hexose\ unit)]^-$, suggesting that **7** is a methyl ester of jalapinolic acid pentaglycoside composed of 1 mol of hexose and 4 mol of methylpentose, and that the hexose combines directly with the aglycone. Acidic hydrolysis of **7** gave (*S*)-jalapinolic acid, D-glucose and L-rhamnose. The nuclear Overhauser effect spectroscopy (NOESY) spectrum of **7** revealed correlation peaks between 2-H of Glc/1-H of Rha, 4-H of Rha/1-H of Rha′, 3-H of Rha′/1-H of Rha″ and 4-H of Rha′/1-H of the fourth rhamnose (Rha‴). The carbon signals due to 2-C of the glucose unit (Glc), 4-C of Rha, and 3-C and 4-C of Rha′ showed glycosylation shifts of 4.7, 6.7, 9.9 and 4.9 ppm, respectively, in comparison with those of the corresponding methyl pyranosides.[12] The chemical shifts and coupling constants of the signals due to the sugar moiety were compatible with the β glycosidic linkage for Glc in $^4C_1$ conformation and α linkages for all the rhamnose units in $^1C_4$ conformation (Table II). Consequently, **7** was characterized as methyl (*S*)-jalapinolic acid 11-*O*-α-L-rhamnopyranosyl-(1→3)-*O*-[α-L-rhamnopyranosyl-(1→4)]-*O*-α-L-rhamnopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranoside, that is, 3‴-*O*-α-L-rhamnopyranoside of operculinic acid E[9] (Fig. 2).

The ^{1}H-NMR spectrum of **2** exhibited signals of the nonequivalent 2-H_2 of Jla along with those of 2-H of (*S*)-2-methylbutyric (Mba) and 2-H_2 of *n*-dodecanoic acid groups (Dodeca) (Table II). Furthermore, compared with the spectrum of **7**, the acylation shifts observed at 2-H (1.41 ppm) of Rha, 2-H (0.98 ppm) of Rha′ and 4-H (1.62 ppm) of Rha‴ indicated the locations of the acyl groups to be 2-OH of Rha, 2-OH of Rha′ and 4-OH of Rha‴. The fragment peaks observed in the negative ion

TABLE II. ^{1}H-NMR Spectral Data for **1**, **2**, **3**, **4**, **5**, **7** and **8** (in Pyridine-d_5)

		1	2	7	3	8	4	5
Fuc	1	4.73 (d, 6.8)			4.72 (d, 7.5)	4.80 (d, 7.9)	4.71 (d, 7.5)	4.71 (d, 7.6)
	2	4.17 (dd, 6.8, 9.2)			4.12 (dd, 7.5, 10.0)	4.00 (dd, 7.9, 9.5)	4.13 (dd, 7.5, 9.5)	4.11 (dd, 7.6, 10.0)
	3	4.06 (dd, 9.2, 3.1)			4.04 (dd, 10.0, 3.5)	4.16 (dd, 9.5, 3.4)	4.04 (dd, 9.5, 3.5)	4.04 (dd, 10.0, 3.5)
	4	4.00 (dd, 3.1, 0.5)			3.97 (br d, 3.5)	3.94 (d, 3.4)	3.97 (d, 3.5)	3.96 (d, 3.5)
	5	3.77 (dq, 0.5, 6.9)			3.76 (q, 6.5)	3.80 (br q, 6.4)	3.75 (q, 6.5)	3.75 (q, 6.5)
	6	1.53 (d, 6.9)			1.50 (d, 6.5)	1.52 (d, 6.4)	1.50 (d, 6.5)	1.49 (d, 6.5)
Glc	1		4.89 (d, 7.8)	4.50 (d, 7.4)				
	2		3.88 (dd, 7.8, 8.7)	4.26 (dd, 7.4, 7.5)				
	3		4.16 (dd, 8.7, 8.6)	4.29 (dd, 7.5, 8.1)				
	4		4.12 (dd, 8.6, 9.1)	4.14 (dd, 8.1, 8.7)				
	5		3.86 (ddd, 9.1, 5.9, 2.7)	3.89 (ddd, 8.7, 5.9, 2.8)				
	6		4.30 (dd, 5.9, 11.8)	4.33 (dd, 5.9, 11.6)				
			4.46 (dd, 2.7, 11.8)	4.40 (dd, 2.7, 11.6)				
Rha	1	5.53 (d, 1.7)	5.57 (d, 1.6)	6.37 (d, 0.9)	5.47 (d, 1.2)	6.25 (br s)	5.46 (d, 2.0)	5.46 (d, 1.2)
	2	5.97 (dd, 1.7, 3.1)	6.05 (dd, 1.6, 3.1)	4.64 (dd, 0.9, 3.1)	5.92 (dd, 1.2, 3.0)	4.64[a]	5.92 (dd, 2.0, 3.0)	5.92 (dd, 1.2, 3.0)
	3	5.05 (dd, 3.1, 9.4)	5.06 (dd, 3.1, 9.6)	4.63 (dd, 3.1, 9.0)	4.98 (dd, 3.0, 9.9)	4.65 (dd, 3.4, 9.5)	4.99 (dd, 3.0, 10.0)	4.99 (dd, 3.0, 9.7)
	4	4.23 (dd, 9.4, 10.3)	4.25 (dd, 9.6, 10.0)	4.36 (dd, 9.0, 8.8)	4.19 (dd, 9.9, 9.9)	4.31 (dd, 9.5, 9.5)	4.19 (dd, 10.0, 9.9)	4.19 (dd, 9.7, 9.9)
	5	4.49 (dq, 10.3, 5.9)	4.36 (dq, 10.0, 6.4)	4.43 (dq, 8.8, 5.8)	4.42 (dq, 9.9, 6.1)	4.88 (dq, 9.5, 6.1)	4.42 (dq, 9.9, 6.5)	4.42 (dq, 9.9, 6.1)
	6	1.73 (d, 5.9)	1.61 (d, 6.4)	1.69 (d, 5.8)	1.61 (d, 6.1)	1.58 (d, 6.1)	1.61 (d, 6.5)	1.60 (d, 6.1)
Rha′	1	6.06 (d, 1.7)	6.13 (d, 1.6)	6.19 (d, 1.6)	6.09 (d, 1.2)	6.19 (d, 1.5)	6.12 (d, 1.5)	6.11 (d, 1.2)
	2	6.08 (dd, 1.7, 3.6)	5.96 (dd, 1.6, 3.2)	4.98 (dd, 1.6, 3.5)	5.96 (dd, 1.2, 3.2)	4.88 (dd, 1.5, 2.0)	5.99 (dd, 1.5, 2.9)	5.98 (dd, 1.2, 3.3)
	3	4.76 (dd, 3.6, 8.8)	4.60 (dd, 3.2, 9.8)	4.55 (dd, 3.5, 9.1)	4.59 (dd, 3.2, 9.5)	4.56 (dd, 2.0, 8.9)	4.58 (dd, 2.9, 9.2)	4.58 (dd, 3.3, 9.0)
	4	4.33 (dd, 8.8, 9.5)	4.27 (dd, 9.8, 9.7)	4.49 (dd, 9.1, 9.4)	4.24 (dd, 9.5, 9.5)	4.48 (dd, 8.9, 8.9)	4.27 (dd, 9.2, 9.2)	4.26 (dd, 9.0, 9.9)
	5	4.42 (dq, 9.5, 6.1)	4.37 (dq, 9.7, 5.8)	4.31 (dq, 9.4, 6.1)	4.34 (dq, 9.5, 6.0)	4.33 (dq, 8.9, 6.4)	4.35 (dq, 9.2, 6.5)	4.32 (dq, 9.9, 5.5)
	6	1.68 (d, 6.1)	1.66 (d, 5.8)	1.58 (d, 6.1)	1.64 (d, 6.0)	1.56 (d, 6.4)	1.64 (d, 6.5)	1.62 (d, 5.5)
Rha″	1	6.22 (d, 1.5)	5.63 (d, 1.4)	5.68 (d, 1.6)	5.71 (d, 1.0)	5.69 (br s)	5.58 (d, 1.0)	5.57 (d, 1.2)
	2	6.27 (dd, 1.5, 3.1)	4.83 (dd, 1.4, 3.1)	4.88 (dd, 1.6, 3.2)	4.81 (dd, 1.0, 3.0)	4.89 (dd, 1.0, 3.4)	4.89 (dd, 1.0, 3.0)	4.78 (dd, 1.2, 2.8)
	3	4.84 (dd, 3.1, 10.2)	4.43 (dd, 3.1, 9.8)	4.55 (dd, 3.2, 9.0)	4.39 (dd, 3.0, 10.0)	4.55 (dd, 3.4, 9.5)	4.45 (dd, 3.0, 9.9)	4.44 (dd, 2.8, 9.9)
	4	5.87 (dd, 10.2, 10.3)	4.23 (dd, 9.8, 9.7)	4.22 (dd, 9.0, 9.2)	4.20 (dd, 10.0, 10.0)	4.25 (dd, 9.5, 9.5)	4.20 (dd, 9.9, 9.9)	4.19 (dd, 9.9, 9.6)
	5	4.53 (dq, 10.3, 5.8)	4.28 (dq, 9.7, 6.2)	4.74 (dq, 9.2, 6.0)	4.34 (dq, 10.0, 6.0)	4.74 (dq, 9.5, 6.1)	4.34 (dq, 9.9, 6.0)	4.30 (dq, 9.6, 5.8)
	6	1.58 (d, 5.8)	1.44 (d, 6.2)	1.61 (d, 6.0)	1.56 (d, 6.0)	1.62 (d, 6.1)	1.58 (d, 6.0)	1.57 (d, 5.8)
Rha‴	1		5.89 (d, 1.2)	5.95 (d, 1.1)	5.89 (d, 1.2)	5.69 (br s)	5.90 (d, 1.0)	5.89 (d, 1.5)
	2		4.72 (dd, 1.2, 3.3)	4.69 (dd, 1.1, 3.2)	4.70 (dd, 1.2, 3.0)	4.69 (dd, 1.0, 3.4)	4.67 (dd, 1.0, 3.4)	4.67 (dd, 1.5, 3.0)
	3		4.51 (dd, 3.3, 9.9)	4.39 (dd, 3.2, 9.6)	4.50 (dd, 3.0, 9.8)	4.37 (dd, 3.4, 9.2)	4.49 (dd, 3.4, 10.0)	4.48 (dd, 3.0, 10.0)
	4		5.83 (dd, 9.9, 9.6)	4.21 (dd, 9.6, 10.0)	5.82 (dd, 9.8, 9.8)	4.22 (dd, 9.2, 9.8)	5.80 (dd, 10.0, 10.0)	5.80 (dd, 10.0, 10.0)
	5		4.39 (dq, 9.6, 5.5)	4.30 (dq, 10.0, 5.6)	4.39 (dq, 9.8, 6.4)	4.34 (dq, 9.8, 6.4)	4.36 (dq, 10.0, 6.4)	4.32 (dq, 10.0, 6.4)
	6		1.59 (d, 5.5)	1.58 (d, 5.6)	1.42 (d, 6.4)	1.56 (d, 6.4)	1.42 (d, 6.4)	1.41 (d, 6.4)
Jla	2	2.27 (ddd, 3.4, 8.0, 14.7)	2.24 (ddd, 3.8, 8.5, 14.9)	2.32 (t, 7.3)	2.22 (ddd, 3.0, 8.0, 15.0)	2.50 (t, 7.3)	2.28 (ddd, 3.0, 7.0, 15.0)	2.25 (ddd, 3.0, 7.0, 15.0)
		2.44 (ddd, 3.4, 8.1, 14.7)	2.39 (ddd, 3.8, 8.7, 14.9)		2.40[a]		2.40	2.40
	11	3.83 (br s)	3.89 (br s)	4.06 (br s)	3.84 (br s)	4.00 (br s)	3.84 (br s)	3.84 (br s)
	16	0.86 (t, 7.0)	0.85 (t, 7.0)	0.92 (t, 7.1)	0.88 (t, 7.0)	0.93 (t, 7.3)	0.89 (t, 7.0)	0.88 (t, 7.0)
Cna	2	6.50 (d, 15.9)						
	3	7.79 (d, 15.9)						
Mba	2		2.47 (tq, 7.0, 7.0)		2.46 (tq, 7.0, 7.0)			
	5		1.08 (d, 7.0)		1.07 (d, 7.0)			
Org	2	2.32	2.39 (ddd, 3.5, 7.5, 7.5)		2.36 (ddd, 3.5, 7.5, 7.5)		2.30 (ddd, 4.0, 7.5, 7.5)	2.29 (ddd, 4.0, 7.5, 7.5)
		2.44 (ddd, 3.0, 7.5, 7.5)					2.45 (ddd, 3.0, 7.5, 7.5)	2.41 (ddd, 3.0, 7.5, 7.5)

δ in ppm from TMS. All the chemical shifts are based on the COSY spectral data. Org: octanoyl, decanoyl or dodecanoyl. *a)* Signals are overlapping.

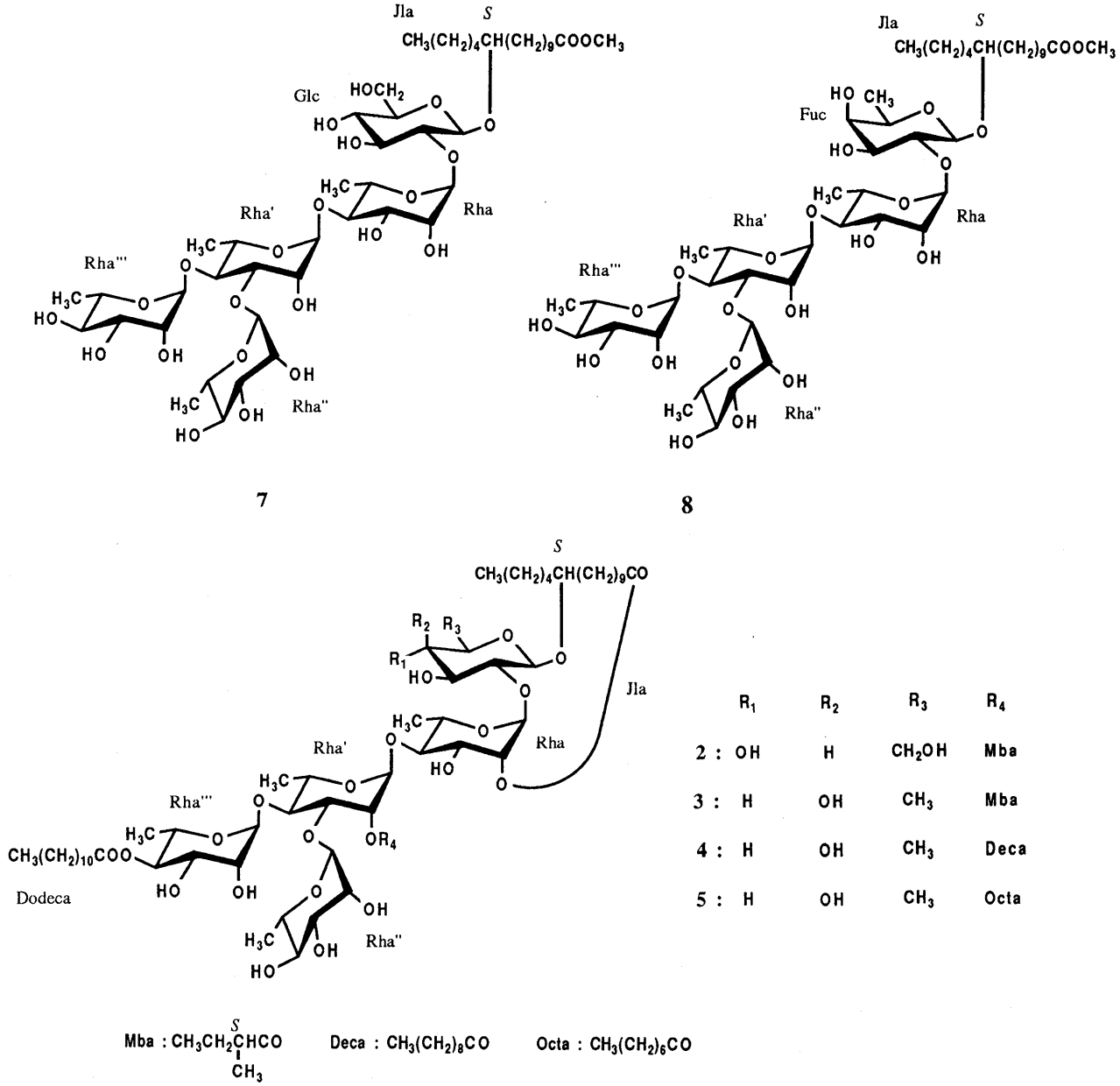

Fig. 2. Structures of **2**—**5**, **7** and **8**

FAB-MS at *m/z* 271 [jalapinolic acid − H]$^-$, 433 [271 + 162 (hexosyl unit)]$^-$ and 561 [433 + 128 (methylpentosyl unit − H_2O)]$^-$ imply that the Jla combines with 2-OH of Rha. In the long range ^1H–^{13}C shift correlation (COLOC) spectrum, the carbonyl carbon signal at δ 175.5 displayed cross peaks with the signals due to 2-CH_3 of Mba and 2-H of Rha′. Thus, the Mba is attached at 2-OH of Rha′ and hence the remaining Dodeca is placed at 4-OH of Rha‴.

Accordingly, the structure of **2** was concluded to be (*S*)-jalapinolic acid 11-*O*-α-L-rhamnopyranosyl-(1→3)-*O*-[4-*O*-*n*-dodecanoyl-α-L-rhamnopyranosyl-(1→4)]-*O*-[2-*O*-(*S*)-2-methylbutyryl]-α-L-rhamnopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranoside, intramolecular 1,2″-ester (Fig. 2).

Simonin III, $C_{63}H_{110}O_{24}$ (**3**), negative ion FAB-MS *m/z*: 1249 [M − H]$^-$, showed, in the ^{13}C-NMR spectrum, the presence of five anomeric and three ester carbonyl carbons (Table I). On alkaline hydrolysis and subsequent methylation, **3** gave methyl (*S*)-2-methylbutyrate, methyl dodecanoate and the methyl ester of a new glycosidic acid named simonic acid B (**8**), $C_{47}H_{84}O_{23}$.

Compound **8** exhibited the [M − H]$^-$ ion peak at *m/z* 1015 in the negative ion FAB-MS and provided D-fucose, L-rhamnose and methyl (*S*)-jalapinolate by hydrolysis in the same manner as for **7**, showing **8** to be a jalapinolic acid pentaglycoside. The NOESY spectrum of **8** demonstrated correlation peaks between 2-H of fucose unit (Fuc)/1-H of Rha, 4-H of Rha/1-H of Rha′, 3-H of Rha′/1-H of Rha″, and 4-H of Rha′/1-H of Rha‴. Moreover, the ^{13}C-NMR spectrum of **8** showed glycosylation shifts of 2.9, 7.1, 10.0 and 4.9 ppm at 2-C of Fuc, 4-C of Rha, and 3-C and 4-C of Rha′ (Table I). The coupling constants and chemical shifts of the signals ascribable to the sugar moiety suggested the mode of glycosidic linkage of Fuc to be β in $^4C_1$ and those of all the rhamnose units to be α in $^1C_4$ conformation (Table II). Consequently, compound **8** was concluded to have the structure shown in Fig. 2, which corresponds to the 3‴-*O*-α-L-rhamnopyranoside of opercu-

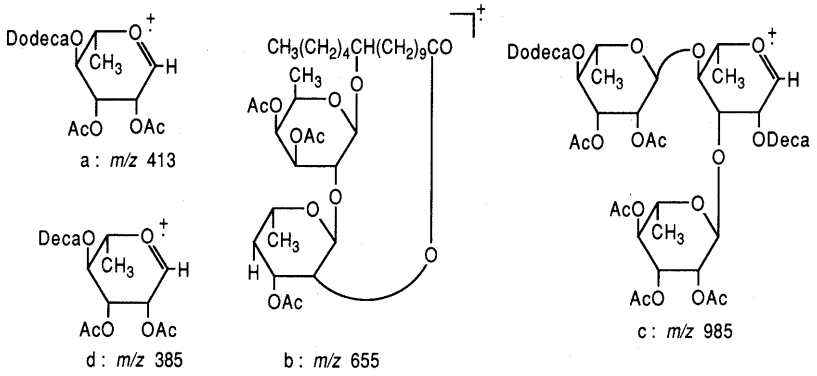

Fig. 3. EI-MS Fragment Ions of **9**

linic acid C (**7**).

The ^{1}H-NMR spectrum of **3**, besides the signals of the nonequivalent 2-H_2 of Jla along with those due to 2-H of Mba and 2-H_2 of Dodeca, exhibited signals ascribable to 2-H of Rha, 2-H of Rha′ and 4-H of Rha‴ which were shifted downfield by 1.28, 1.08 and 1.60 ppm, respectively (Table II). Further, its negative ion FAB-MS showed fragment peaks at *m/z* 271 $[\text{jalapinolic acid}-\text{H}]^-$, 417 $[271+146]^-$ and 545 $[417+128\ (146-H_2O)]^-$. The carboxyl group of Jla is therefore linked with 2-OH of Rha. In the COLOC spectrum, the carbonyl carbon signal at δ 175.5 was correlated with the ^{1}H signals due to 2-CH_3 of Mba and 2-H (δ 5.96) of Rha′. The Mba and Dodeca are thus located at 2-OH of Rha′ and 4-OH of Rha‴, respectively.

Accordingly, **3** was characterized as (*S*)-jalapinolic acid 11-*O*-α-L-rhamnopyranosyl-(1→3)-*O*-[(4-*O*-*n*-dodecanoyl)-α-L-rhamnopyranosyl-(1→4)]-*O*-[2-*O*-(*S*)-2-methylbutyryl]-α-L-rhamnopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-fucopyranoside, intramolecular 1, 2″-ester (Fig. 2).

Simonin IV (**4**), $C_{68}H_{120}O_{24}$, yielded *n*-decanoic, *n*-dodecanoic acids and **8** upon alkaline hydrolysis. The negative ion FAB-MS exhibited the same fragment peaks at *m/z* 271, 417 and 545 as those of **3**, along with the $[\text{M}-\text{H}]^-$ ion peak at *m/z* 1319. The ^{1}H-NMR signals due to the sugar moiety were almost superimposable on those of **3** (Table II). From these data, **4** was considered to be an analogue of **3** in that the Mba of **3** is simply replaced by a Deca. As the locations of the organic acid groups could not be determined by a COLOC experiment, the electron impact mass spectrum (EI-MS) of the octaacetate of **4** (**9**) was recorded. In the spectrum, though fragment peaks ascribable to a, b and c were seen at *m/z* 413 (a), 655 (b) and 985 (c), no peak at *m/z* 385, expected if the location of Deca is in Rha″ (d), was observed (Fig. 3). The Deca and Mba are therefore placed at 2-OH of Rha′ and 4-OH of Rha‴, respectively. Consequently, the structure of **4** was concluded to be as shown in Fig. 2.

Simonin V (**5**), $C_{66}H_{116}O_{24}$, negative ion FAB-MS *m/z*: 1291 $[\text{M}-\text{H}]^-$), was analyzed to consist of *n*-dodecanoic and *n*-octanoic acids and **8**. The proton and carbon signals owing to the sugar moiety were quite similar to those of **3**, showing the acyl groups to be attached at 2-OH of Rha, 2-OH of Rha′ and 4-OH of Rha‴ (Tables I and II). The EI-MS of the peracetate of **5** (**10**) revealed that the ester linkages of the Jla, Dodeca and *n*-octanoic acid groups (Octa) are placed at 2-OH of Rha, 2-OH of Rha′ and 4-OH of Rha‴, respectively. Consequently, the structure of simonin V (**5**) was concluded to be as shown in Fig. 2.

It is noteworthy that simonin I is the first example of a resin glycoside with an aromatic acid, *trans*-cinnamic acid, as a component organic acid.

Experimental

General Procedures All instruments and materials used were the same as those cited in the preceding report[1] unless otherwise specified. The HMBC spectrum was recorded by use of a GE NMR Omega machine (500 MHz). Specific rotations were determined at 20±2 °C.

Preparation of Jalapin Fraction The powdered dry roots (13 kg) of *I. batatas* (L.) LAM. (cv. Simon) cultivated in the garden of this university were extracted with $CHCl_3$ (15 l×2) at room temperature and the solution was concentrated *in vacuo* to give a brown powder (26 g). This was partitioned between *n*-hexane (100 ml) and MeOH (100 ml). The MeOH soluble portion was concentrated *in vacuo* to give a crude jalapin fraction (21.2 g).

Characterization of the Component Organic and Glycosidic Acids of Jalapin Fraction The jalapin fraction (926 mg) was dissolved in 5% KOH (20 ml) and heated at 90 °C for 3 h. The reaction mixture was acidified to pH 4.0 and shaken with ether (20 ml). The ether layer was reduced to give an oil (fr. 1, 110 mg). The water layer was passed through MCI gel CHP 20P (H_2O→acetone) and the acetone eluate was concentrated to afford a brown powder (fr. 2, 720 mg).

Fraction 1 (*ca.* 1 mg) was examined by GC [condition 1: column, Unisole 30T (5%), 2 m×3.2 mm, carrier gas, N_2 (1.5 kg/cm^2 (117 ml/min)); column temperature, 130 °C], t_R (min): 3.44 (isobutyric acid), 4.65 (*n*-butyric acid), 5.89 (2-methylbutyric acid), 14.99 (tiglic acid). Fraction 1 (*ca.* 1 mg) was methylated with diazomethane and the mixture was analyzed by GC [condition 2: column, Silicone OV-1 (1%), 2 m×3.2 mm; carrier gas, N_2 (1.5 kg/cm^2 (117 ml/min)); column temperature, 130 °C), t_R (min): 1.60 (methyl *n*-octanoate), 3.89 (methyl *n*-decanoate), 9.72 (methyl *trans*-cinnamate), 11.16 (methyl *n*-dodecanoate).

Determination of the Absolute Configuration of 2-Methylbutyric Acid Fraction 1 (100 mg) was distilled (70 °C (20 mmHg)) to give an oil (8 mg). One drop of $SOCl_2$ was added to a solution of the oil (3 mg) in dry benzene (1 ml). The solution was refluxed for 15 min then (*S*)-(−)-1-phenylethylamine (10 μl) was added. The reaction mixture was refluxed for 30 min, then poured into ice water (3 ml) and extracted with EtOAc (3 ml). The EtOAc layer was washed with 0.1 N HCl (3 ml), 5% $NaHCO_3$ (3 ml) and water (3 ml), successively. The EtOAc layer was evaporated *in vacuo* to give an oily residue (5 mg). It was chromatographed on silica gel (EtOAc–*n*-hexane, 1:4) to give a white powder (4 mg), mp 86 °C, EI-MS *m/z*: 205 $[\text{M}]^+$. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 7.25—7.32 (5H, arom H), 5.70 (1H, br s, NH), 5.15 (1H, dq, J=7.0, 7.0 Hz), 2.09 (1H, ddq, J=7.0, 7.0, 7.0 Hz, 2-H), 1.65, 1.41 (each 1H, ddq, J=15.0, 7.0, 7.5 Hz, 3-H_2), 1.48 (3H, d, J=7.0 Hz, 2-CH_3), 1.14 (3H, d, J=7.0 Hz, CH_3), 0.86 (3H, t, J=7.5 Hz, 3-CH_3). This was analyzed by HPLC (column, Chemcosorb 5-Si, 2.1 mm×250 mm, flow rate, 2 ml/min; detector, UV (254 nm); solvent, EtOAc–*n*-hexane, 1:4) to show peaks at t_R (min): 13.99 ((*S*)-(−)-*N*-1-phenylethyl-(*S*)-(+)-2-methylbutyramide) [*cf.* 12.06 (*S*)-(−)-*N*-1-phenylethyl-(*R*)-(−)-2-methylbutyramide].

Acidic Hydrolysis of Fr. 2 Fraction 2 (100 mg) was dissolved in 1 N

H_2SO_4 (5 ml) and heated at 90 °C for 3 h. The reaction mixture was extracted with ether. The ether layer was concentrated *in vacuo* to give colorless needles (12 mg), mp 62 °C. This product (12 mg) was treated with diazomethane in ether to give needles (13 mg), mp 43 °C, which were identical with authentic methyl (*S*)-jalapinolate[13] on GC (condition 3: column, Silicone OV-17 (2%), 3.2 mm i.d. × 2 m; carrier gas, N_2 (1.5 kg/cm^2); column temperature, 190 °C).

A solution of the methyl ester (10 mg) and (−)-α-methoxy-α-trifluoromethylphenylacetyl (MTPA) chloride (25 mg) in pyridine (0.5 ml) was stirred for 17 h at room temperature. After removal of the solvent under a stream of N_2, the residue was chromatographed on silica gel to give an MTPA ester (16 mg). ^{1}H-NMR ($CDCl_3$) δ: 0.840 (3H, t, J=6.9 Hz, 16-H_3), 2.299 (2H, t, J=7.5 Hz, 2-H_2), 3.556 (3H, q, J=1.2 Hz, OCH_3), 3.663 (3H, s, $COOCH_3$), 5.083 (1H, tt, J=5.5, 6.7 Hz, 11-H). Its ^{1}H-NMR spectrum ($CDCl_3$) was superimposable on that of the (−)-MTPA ester of methyl (*S*)-jalapinolate.[13]

The aqueous layer was neutralized with 5% KOH and desalted by chromatography over LH-20 (MeOH) to give a sugar mixture (35 mg). The mixture (8 mg) was subjected to GC analysis as the trimethylsilyl (TMS) ethers of the methyl thiazolidine (*R*)-2-carboxylate derivatives according to Hara *et al.*[7] GC (column, a fused silica gel capillary column Bonded MPS-50 (Quadrex), 0.25 mm i.d. × 50 m, 0.25 μm film thickness; carrier gas, He (30 ml/min); column temperature, 220 °C), t_R (min): 18.86 (D-quinovose), 19.52 (L-rhamnose), 21.01 (D-fucose), 27.07 (D-glucose).

Isolation of Simonins I (1)—V(5) The jalapin fraction (20.0 g) was passed through Sephadex LH-20 column (MeOH) to furnish fr. 3 (14.6 g) and fr. 4 (5.0 g). Column chromatography over silica gel ($CHCl_3$–MeOH–H_2O, 13 : 1 : 0.1→7 : 1 : 0.1→MeOH) of fr. 3 gave fr. 5 (2.77 g), fr. 6 (2.46 g), fr. 7 (4.5 g), fr. 8 (3.31 g) and fr. 9 (1.58 g). Fraction 6 was subjected to preparative HPLC on an Inertsil ODS-2 column (6 mm i.d. × 250 mm, GL Sciences Co., Ltd., 87% MeOH) to give **1** (9.8 mg), a white powder, mp 114—116 °C, $[\alpha]_D$ −9.3° (c=0.2, MeOH). Negative ion FAB-MS m/z (relative intensity): 1275 (4) $[M-H]^-$, 1145 (5) $[M-H-130\ (Cna)]^-$, 837 (9) $[1145-154\ (Deca)\times 2]^-$, 691 (11) $[837-146\ (methylpentose\ unit)]^-$, 545 (11) $[691-146]^-$, 417 (100) $[545-146+18\ (H_2O)]^-$, 271 (52) $[417-146,\ jalapinolic\ acid\ unit]^-$. *Anal.* Calcd for $C_{69}H_{112}O_{21}$: C, 64.87; H, 8.84. Found: C, 64.21; H, 8.92. ^{1}H-NMR (pyridine-d_5) δ: see Table II. ^{13}C-NMR (pyridine-d_5) δ: see Table I.

Similar preparative HPLC (Inertsil ODS-2, MeOH) of fr. 9 gave **2** (21.6 mg), a white powder, mp 121—123.5 °C, $[\alpha]_D$ −27.8° (c=1.0, MeOH). Negative ion FAB-MS m/z: 1265 (67) $[M-H]^-$, 1181 (9) $[M-H-84\ (Mba)]^-$, 1083 (14) $[M-H-182\ (Dodca)]^-$, 853 (8) $[1083-84-146]^-$, 561 (78) $[853-146\times 2]^-$, 433 (100) $[561-146+18]^-$, 271 (81) $[433-162\ (hexose\ unit)]^-$. *Anal.* Calcd for $C_{63}H_{110}O_{25}$: C, 59.74; H, 8.67. Found: C, 59.16; H, 8.90. ^{1}H-NMR (pyridine-d_5) δ: see Table II. ^{13}C-NMR (pyridine-d_5) δ: see Table I.

Preparative HPLC (Hibar column RP-18, Merck, 4 mm i.d. × 25 cm, MeOH) of fr. 8 (3.3 g) to give **3** (46 mg), **4** (146 mg) and **5** (37.9 mg). **3**: a white powder, mp 127−132 °C, $[\alpha]_D$ −37.5° (c=1.0, MeOH). Negative ion FAB-MS m/z: 1249 (69) $[M-H]^-$, 545 (77) $[271\ (jalapinolic\ acid\ unit)+146\times 2-18]^-$, 417 (100) $[271+146]^-$, 271 (83). *Anal.* Calcd for $C_{63}H_{110}O_{24}$: C, 60.46; H, 8.86. Found: C, 60.86; H, 8.90. ^{1}H-NMR (pyridine-d_5) δ: see Table II. ^{13}C-NMR (pyridine-d_5) δ: see Table I. **4**: a white powder, mp 123−125°C, $[\alpha]_D$ −43.3° (c=1.0, MeOH). Negative ion FAB-MS m/z: 1319 (48) $[M-H]^-$, 1165 (10) $[M-H-154\ (decanoyl\ unit)]^-$, 1137 (6) $[M-H-182]^-$, 837 (9) $[1137-154-146]^-$, 691 (3) $[837-146]^-$, 545 (67) $[691-146]^-$, 417 (100) $[545-146+18]^-$, 271 (99). *Anal.* Calcd for $C_{68}H_{120}O_{24}$: C, 61.80; H, 9.15. Found: C, 61.20; H, 9.14. ^{1}H-NMR (pyridine-d_5) δ: see Table II. ^{13}C-NMR (pyridine-d_5) δ: see Table I. **5**: a white powder. mp 115—116 °C, $[\alpha]_D$ −35.2° (c=1.0, MeOH). Negative ion FAB-MS m/z: 1291 (48) $[M-H]^-$, 545 (65), 417 (100), 271 (95). *Anal.* Calcd for $C_{66}H_{116}O_{24}$: C, 61.28; H, 9.04. Found: C, 61.08; H, 8.90. ^{1}H-NMR (pyridine-d_5) δ: see Table II. ^{13}C-NMR (pyridine-d_5) δ: see Table I.

Alkaline Hydrolysis of 1—5 Compounds **1—5** (6—10 mg) were each dissolved in 5% KOH (5 ml) and heated at 90 °C for 2 h. The reaction mixture was adjusted to pH 4.0 and extracted with ether (5 ml × 2). The ether layer was analyzed by GC (condition 1), t_R (min): 5.89 (2-methylbutyric acid) from **2** and **3**. Concentrated aliquots were treated with diazomethane in ether and the reaction mixture was analyzed by GC (condition 2), t_R (min): 1.60 (methyl *n*-octanoate) from **5**, 3.89 (methyl *n*-decanoate) from **1** and **4**, 9.72 (methyl *trans*-cinnamate) from **1**, 11.16 (methyl *n*-dodecanoate) from **2**, **3**, **4** and **5**.

Each aqueous layer was desalted by column chromatography on MCI gel CHP-20P and then the solvent was removed *in vacuo*. The residue was dissolved in MeOH (0.5 ml) and treated with diazomethane in ether to give **6** (3 mg) from **1**, **7** (4 mg) from **2** and **8** (each 5 mg) from **3**, **4** and **5**. **6**: a white powder, mp 100—103 °C, $[\alpha]_D$ −92.0° (c=0.1, MeOH). Its ^{1}H- and ^{13}C-NMR (pyridine-d_5) spectra were respectively superimposable on those of operculinic acid C methyl ester.[8] **7**: a white powder, mp 120—122°C, $[\alpha]_D$ −118.3° (c=1.0, MeOH). Negative ion FAB-MS m/z: 1031 (100) $[M-H]^-$, 885 (49) $[M-H-146]^-$, 739 (11) $[885-146]^-$, 593 (27) $[739-146]^-$, 415 (51) $[593-146-32\ (MeOH)]^-$, 253 (24) $[415-162]^-$. *Anal.* Calcd for $C_{47}H_{84}O_{24}$: C, 54.63; H, 8.19. Found: C, 54.60; H, 8.20. ^{1}H-NMR (pyridine-d_5) δ: see Table II. ^{13}C-NMR (pyridine-d_5) δ: see Table I. **8**: a white powder, mp 112—115 °C, $[\alpha]_D$ −82.0° (c=1.0, MeOH). Negative ion FAB-MS m/z: 1015 (100) $[M-H]^-$, 869 (36) $[M-H-146]^-$, 723 (13) $[869-146]^-$, 577 (28) $[723-146]^-$, 399 (69) $[577-146-32]^-$, 253 (22) $[339-146]^-$. *Anal.* Calcd for $C_{47}H_{84}O_{23}$: C, 55.49; H, 8.32. Found: C, 55.27; H, 8.50. ^{1}H-NMR (pyridine-d_5) δ: see Table II. ^{13}C-NMR (pyridine-d_5) δ: see Table I.

Acidic Hydrolysis of 7 and 8 Each of **7** (15 mg) and **8** (18 mg) was treated in the same manner as described for fr. 2 to give needles (3 mg from **7**), (3 mg from **8**). They were identical with an authentic sample of methyl (*S*)-jalapinolate on GC (condition 3). The sugar fraction was analyzed by GC according to Hara *et al.*,[7] t_R (min): 19.59 (L-rhamnose) and 27.07 (D-glucose) from **7**, 19.60 (L-rhamnose) and 21.01 (D-fucose) from **8**.

Acetylation of 4 and 5 Usual acetylation of **4** (4 mg) and **5** (4 mg) in Ac_2O–pyridine (each 0.5 ml) yielded **9** (5 mg) and **10** (4 mg), respectively. **9**: mp 87—89 °C, $[\alpha]_D$ −10.8° (c=0.4, MeOH). ^{1}H-NMR (pyridine-d_5) δ: 1.99, 2.01, 2.02, 2.06, 2.09, 2.10, 2.34, 2.36 (each 3H, s, $OCOCH_3$). EI-MS m/z: 273 (90), 413 (100), 655 (15), 985 (9). **10**: mp 78—80 °C, $[\alpha]_D$ −17.6° (c=0.3, MeOH). ^{1}H-NMR (pyridine-d_5) δ: 2.00, 2.01, 2.02, 2.07, 2.10, 2.11, 2.35, 2.37 (each 3H, s, $OCOCH_3$). EI-MS m/z: 273 (95), 413 (100), 655 (12), 957 (10).

Acknowledgment We thank Professor T. Nohara of Kumamoto University for supplying the young plants of *I. batatas* (L.) LAM. (cv. Simon) and Mr. M. Nishi and Mr. S. Inoue of this university for measurements of the NMR spectra, MS and elemental analyses. Thanks are also due to Dr. M. Oyabu of Shimadzu Co. for measurement of the HMBC spectrum.

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